

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 17 May 2001 (17.05.01)	
International application No. PCT/NL00/00626	Applicant's or agent's file reference BO 42963 ABA
International filing date (day/month/year) 06 September 2000 (06.09.00)	Priority date (day/month/year) 06 September 1999 (06.09.99)
Applicant VERHAAK, Michael, Johannes, Franciscus, Maria	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 05 April 2001 (05.04.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference BO 42963 ABA	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/NL 00/ 00626	International filing date (day/month/year) 06/09/2000	(Earliest) Priority Date (day/month/year) 06/09/1999
Applicant STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

REDUCTION OF N2O EMISSIONS

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☒ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

NL 00/00626

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 99 49954 A (STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND) 7 October 1999 (1999-10-07) cited in the application the whole document	1-8
A	US 5 524 432 A (JAMES G. HANSEL) 11 June 1996 (1996-06-11) column 7, line 15 - line 35	1-8
A	DE 41 28 629 A (BASF) 4 March 1993 (1993-03-04) the whole document	1-8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

16 February 2001

Date of mailing of the international search report

23/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bogaerts, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

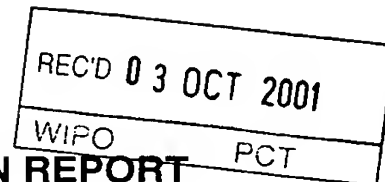
International Application No

P/NL 00/00626

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9949954	A	07-10-1999	NL 1008746 C	01-10-1999
			AU 3173299 A	18-10-1999
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US 5524432	A	11-06-1996	US 5451385 A	19-09-1995
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			CN 1081931 A	16-02-1994
			EP 0582743 A	16-02-1994
			FI 923932 A	14-02-1994
			JP 6086915 A	29-03-1994
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			MX 9205218 A	28-02-1994
			NZ 244172 A	26-10-1994
			PT 100864 A	28-02-1994
			ZA 9206819 A	08-03-1994
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			AU 2058692 A	04-02-1993
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			MX 9204495 A	01-02-1993
			NZ 243726 A	26-10-1994
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			WO 9304774 A	18-03-1993
			EP 0600962 A	15-06-1994
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			FI 940915 A	25-02-1994
			JP 6509984 T	10-11-1994
			NO 940653 A	25-02-1994
			PL 169899 B	30-09-1996
			SK 23194 A	09-11-1994
			US 5612009 A	18-03-1997
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference BO 42963 Bot		FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/NL00/00626	International filing date (day/month/year) 06/09/2000	Priority date (day/month/year) 06/09/1999	
International Patent Classification (IPC) or national classification and IPC B01D53/86			
Applicant STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 05/04/2001	Date of completion of this report 03.10.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Bogaerts, M Telephone No. +31 70 340 2335 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00626

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-8 as originally filed

Claims, No.:

1-8 as originally filed

Drawings, sheets:

1/2-2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL00/00626

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-8
	No: Claims
Inventive step (IS)	Yes: Claims 1-8
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-8
	No: Claims

2. Citations and explanations
see separate sheet

Ad V:

None of the available prior art documents disclose the selective reduction of N_2O in the presence of a solid catalyst, with the addition of a saturated hydrocarbon as reducing agent where the catalyst is a promoted iron-containing zeolite.

Applicant has demonstrated (in the examples) a surprising effect by the distinguishing features. The claimed solution to the problem of enabling a more selective reduction of N_2O is not obvious.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BO 42963 Bot	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/NL00/00626	International filing date (day/month/year) 06/09/2000	Priority date (day/month/year) 06/09/1999	
International Patent Classification (IPC) or national classification and IPC B01D53/86			
Applicant STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


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- IV ☐ Lack of unity of invention
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- VI ☐ Certain documents cited
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- VIII ☐ Certain observations on the international application

Date of submission of the demand 05/04/2001	Date of completion of this report 03.10.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Bogaerts, M Telephone No. +31 70 340 2335



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00626

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

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Claims, No.:

1-8 as originally filed

Drawings, sheets:

1/2-2/2 as originally filed

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- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

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- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
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- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL00/00626

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

**2. Citations and explanations
see separate sheet**

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL00/00626

Ad V:

None of the available prior art documents disclose the selective reduction of N_2O in the presence of a solid catalyst, with the addition of a saturated hydrocarbon as reducing agent where the catalyst is a promoted iron-containing zeolite.

Applicant has demonstrated (in the examples) a surprising effect by the distinguishing features. The claimed solution to the problem of enabling a more selective reduction of N_2O is not obvious.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21288 A1

(51) International Patent Classification⁷: **B01D 53/86**

(21) International Application Number: **PCT/NL00/00626**

(22) International Filing Date:
6 September 2000 (06.09.2000)

(25) Filing Language: **Dutch**

(26) Publication Language: **English**

(30) Priority Data:
1012983 6 September 1999 (06.09.1999) NL
1013862 15 December 1999 (15.12.1999) NL

(71) Applicant (for all designated States except US): **STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND** [NL/NL]; Westerduinweg 3, NL-1755 LE Petten (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **VERHAAK, Michael, Johannes, Franciscus, Maria** [NL/NL]; Westerweg 41, NL-1815 DB Alkmaar (NL).

(74) Agent: **JORRITSMA, Ruurd**; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **REDUCTION OF N₂O EMISSIONS**

(57) Abstract: The invention relates to a method for the selective catalytic reduction of nitrous oxide (N₂O) in the presence of a solid catalyst, with the addition of a saturated hydrocarbon as reducing agent. The invention is characterized in that the catalyst used is a promoted, iron-containing zeolite. As a result, it is possible to increase the conversion of (NO₂) compared to unpromoted iron-containing zeolite catalysts. The promoted catalyst according to the invention is active at temperatures below 350 °C. Furthermore, it has been found that the iron-containing zeolite catalysts which are promoted with precious metal also give low emissions of CO and residual hydrocarbons. The catalyst is also very active under high process pressures and in the presence of sulphur.

WO 01/21288 A1

Reduction of N₂O emissions

Background

5 Nitrous oxide (dinitrogen oxide, N₂O) makes a substantial contribution to the greenhouse effect. The global warming potential (the extent to which a molecule contributes to the greenhouse effect compared to one molecule of CO₂) of N₂O is approx. 310. For a number of years, the policy of reducing emissions of greenhouse gases has been developed. The present invention can make a significant contribution to
10 this policy. Various significant sources of N₂O emissions have been identified: agriculture, industrial production of nylon precursors (adipic acid and caprolactam), the production of nitric acid and motor vehicles fitted with a three-way catalyst.

In principle, various catalytic and non-catalytic techniques can be employed in order to render nitrous oxide harmless. Various catalysts are known for the direct
15 catalytic decomposition of N₂O to N₂ and O₂ (cf. the literature summary provided by Kapteijn et al., Appl. Catal. B9 (1996), pp 25-64 and US-A-5,171,553). However, this reaction is hampered to a considerable extent by the presence of oxygen and water, which are to be found in the off-gases from virtually all the N₂O sources listed above. Selective catalytic reduction is a promising alternative. Various catalysts for the
20 conversion of N₂O with the aid of olefins (C_nH_{2n}), alcohols or ammonia have been studied in the literature (recently: Mauzevin et al. Appl. Catal. B23 (1999) L79-L82 and Pophal et al. Appl Catal. B16 (1998) pp. 177-186 and the literature cited therein). Catalysts employed are often zeolites which have been substituted with a transition metal, such as iron, cobalt or copper.

25 For both technical and economic reasons, the addition of saturated hydrocarbons (C_nH_{2n+2}) would be preferable to the abovementioned reducing agents. Natural gas (CH₄) and LPG (mixture of C₃H₈ and C₄H₁₀) are particularly attractive in this context. It is important that the formation and emission of carbon monoxide (CO) and emission of unreacted hydrocarbons be minimized.

30 The present invention relates to a catalyst which enables N₂O to be converted into nitrogen at a relatively low temperature and which allows very low emissions of CO and hydrocarbons to be achieved.

Prior art

35 International Patent Application WO 9949954 has described a method for the catalytic reduction of N₂O in the presence of a zeolite with the addition of a reducing agent, the reducing agent used being a saturated hydrocarbon, such as methane (CH₄), propane (C₃H₈), LPG (C₃H₈/C₄H₁₀), or a combination of these reducing agents. It has

been found that complete conversion of N_2O can be achieved at reaction temperatures of $400^\circ C$ or lower, even with very low concentrations of the reducing agent and in the presence of water vapour, oxygen and sulphur dioxide. The catalyst involves a specially prepared iron-substituted zeolite.

5 Japanese patent publications JP 05103953 and JP 07213864 describe the removal of N_2O in the presence of, respectively, methane and propane with the aid of (inter alia) an iron-zeolite catalyst. However, these methods take no account of the emission of CO and unreacted hydrocarbons.

10 To prevent undesirable emission of CO and residual hydrocarbons, Japanese patent publication JP 09000884 describes the mechanical mixing of an iron-zeolite catalyst with a supported platinum or palladium catalyst. The N_2O conversion is around 60% at $450^\circ C$ in a gas which contains oxygen and water. The conversion of N_2O achieved with the mechanically mixed catalyst is significantly worse than with the iron-zeolite catalyst alone.

15 JP 05103953, JP 07213864 and JP 09000884 all lack information about the effectiveness of the invention under pressure and/or in the presence of sulphur compounds. This is essential for use in the production of nitric acid and caprolactam, respectively.

20 **Discovery of a novel catalyst**

One object of the present invention is to provide a method for the removal of N_2O from industrial gas streams which contain O_2 , H_2O , NO_x and possibly sulphur and which may be at elevated pressure. A further object of the present invention is to bring about the abovementioned removal of N_2O by the addition of saturated hydrocarbons at a reaction temperature of lower than $400^\circ C$, with very low emissions of CO and unreacted hydrocarbons.

25 To this end, the method according to the invention is characterized in that the catalyst used is a promoted, iron-containing zeolite. The zeolite catalyst is preferably promoted with a precious metal.

30 The use of an iron-containing zeolite catalyst which has been promoted preferably with precious metal (Rh, Pd, Ru, Pt, Au, etc.) in the SCR of N_2O with the aid of saturated hydrocarbons (C_nH_{2n+2}) has surprisingly led to increased conversion of N_2O compared to an unpromoted iron-containing zeolite catalyst. The promoted catalyst is active at temperatures of below $350^\circ C$.

35 Furthermore, it has been found that the iron-containing zeolite catalyst which has been promoted with precious metal reduces the emissions of CO and residual

hydrocarbons very considerably at the operating temperature compared to an unpromoted iron-containing zeolite catalyst.

In addition, it has been found that the catalyst according to the invention is also active in the removal of nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$). This is important in view of the fact that NO_x are also released from the various sources of N_2O .

It has also been found that the catalyst described is also very active in the desired conversion at elevated process pressure, at which it is even more active than at atmospheric pressure. This is an important fact with regard to its application in the nitric acid industry.

Finally, it has been found that the catalyst described is active if sulphur is present in the feed. This is an important fact in connection with its application in the nylon industry.

The invention will be explained in more detail with reference to the following examples together with the associated figures, in which:

Figure 1 shows the degree of conversion of N_2O as a function of temperature for four iron-containing zeolite catalysts promoted with precious metal (A, D, E and F). For comparison purposes, the N_2O conversion achieved by an unpromoted iron-containing zeolite catalyst (X) is also shown. The test conditions are described in Table 2 ($\text{SV} = 19,500 \text{ h}^{-1}$, pressure = 3 bara, C_3H_8 concentration = 1900 ppmv).

Figure 2 shows the CO emissions which occur during the conversion of N_2O using the same catalysts and under the same conditions as in Figure 1.

I. Preparation of the catalysts

The catalysts according to the present invention are produced by adding zeolite Na-ZSM-5 or NH_4 -ZSM-5 to a solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Mohr's salt). After they have been combined, ion exchange is carried out for 8 hours at 80°C . The resulting suspension is filtered, the solid material is washed, is dried at 80°C and is calcined at 550°C .

The Fe-ZSM-5 base material obtained in this way is then impregnated with a volume of a solution of a precious metal precursor in demineralized water which is such that the pores of the base material are precisely filled (so-called incipient wetness impregnation). The concentration of the precious metal precursor is set in such a manner that the desired quantity of precious metal on the base material is obtained. Finally, the catalyst is dried at 80°C and calcined at 550°C . The catalyst powder obtained is pressed into a tablet, is ground and is screened.

The following catalysts are used in the examples:

Table 1

Catalyst	Base	Precious metal
A	Fe-ZSM-5 from Mohr's salt	0.05% Pd
B	Fe-ZSM-5 from Mohr's salt	0.1% Pd
C	Fe-ZSM-5 from Mohr's salt	0.3% Pd
D	Fe-ZSM-5 from Mohr's salt	0.3% Rh
E	Fe-ZSM-5 from Mohr's salt	0.3% Ru
F	Fe-ZSM-5 from Mohr's salt	0.3% Au
X	Fe-ZSM-5 from Mohr's salt	none

II. Test apparatus

The conversion of N_2O by means of SCR using propane and methane was
 5 studied in an automated flow arrangement. The gases N_2 , air, N_2O , C_3H_8 , CH_4 ,
 NO , NO_2 are introduced by means of calibrated mass flow controllers (Brooks). Water
 is added via a Liquiflow controller and a controlled Evaporator Mixer (Bronkhorst).
 The gases emerging are analysed by means of a calibrated FTIR spectrophotometer
 (Elsag, Bailey, Hartmann & Brown, type MB 100). The catalyst is in a stainless steel
 10 reactor. The gases are passed through a preheating section before they come into
 contact with the catalyst. The temperature at the entry to and exit from the catalyst bed
 is measured using thermocouples. The mean of these two temperatures is shown in the
 results of the tests. The pressure in the test arrangement can be set at levels of between
 1 and 5 bar absolute (bara).

The gas composition in the examples is representative for use of the catalyst according to the present invention in the nitric acid industry. The general test conditions are as follows:

Table 2

Weight of catalyst	6 – 15 g
Screening fraction	0.71 – 1.4 mm
Volume of catalyst	10 – 23 ml
Total gas flow rate	5 – 7.5 l/min (STP)
Space velocity	13,000 – 45,000 h ⁻¹
Total pressure	1 – 5 bara
Temperature of catalyst	150 – 500 °C
O ₂ concentration	2.5% v/v
H ₂ O concentration	0.5% v/v
N ₂ O concentration	1500 ppmv
C ₃ H ₈ concentration	1500 – 2500 ppmv
NO ₂ concentration	100 ppmv
NO concentration	100 ppmv

5

III. Influence of the addition of precious metal to iron-containing zeolite

Figure 1 shows the N₂O conversion curves for the catalyst from Table 1 (test conditions as in Table 2, SV = 19,500 h⁻¹, pressure = 3 bara, C₃H₈ concentration = 1900 ppmv). The promoted catalyst (A,D,E,F) are more active than the unpromoted iron-containing zeolite catalyst X. This is evident from the shift of the N₂O conversion curves towards a lower temperature compared to the unpromoted Fe-ZSM-5 catalyst X.

10

Figure 2 shows the CO concentrations as a function of temperature for the same catalysts under the same conditions. When using catalyst X and catalyst F, CO is

formed throughout the entire temperature range. The other catalysts are excellent at eliminating CO emissions: if catalyst E is used, the amount of CO at over 350°C is lower than 10 ppmv, and with catalysts A and D this level is already achieved from 300°C.

- 5 Comparative tests between catalyst A (containing 0.05% Pd) and catalysts B and C (respectively containing 0.1% and 0.3% Pd) reveal similar curves for both N₂O conversion and CO formation. This means that a low concentration of precious metal is sufficient, reducing the cost of the catalyst.

- 10 Table 3 shows the concentrations of the compounds which leave the reactor at a mean temperature of 350°C for a number of catalysts (test conditions as in Table 2, SV = 19,500 h⁻¹, pressure = 3 bara, C₃H₈ concentration = 1900 ppmv).

Table 3

Catalyst	N ₂ O (ppmv)	C ₃ H ₈ (ppmv)	CO (ppmv)	NO _x ^a (ppmv)
C	70	62	3	85
D	55	33	1	85
E	130	75	37	82
F	42	70	2180	45
X	123	167	2267	46

^aNO_x = NO + NO₂

- 15 For all the catalysts, the N₂O and C₃H₈ conversion levels are higher than 90% at 350°C. For the catalysts which contain Pd and Rh, the CO emission is negligible. Another surprise is that the catalysts also remove from 60 to 75% of the NO_x.

IV. Activity of the promoted iron-containing zeolite catalysts at increased process pressure and space velocity

- 20 Increasing the process pressure has a beneficial affect on the activity of the catalysts. Table 4 shows the concentrations of a number of components of the emerging gas, at 1, 3 and 5 bara and at a reaction temperature of 350°C (test conditions as in Table 2, catalyst A, SV = 19,500h⁻¹, C₃H₈ concentration = 1900 ppmv). The N₂O

conversion level remains greater than 90%, while propane slippage, CO and NO_x emissions fall as the process pressure rises.

Table 4

Pressure (bara)	N ₂ O (ppmv)	C ₃ H ₈ (ppmv)	CO (ppmv)	NO _x ^a (ppmv)
1	95	200	14	137
3	128	124	3	135
5	100	54	2	122

^aNO_x = NO + NO₂

5

At a process pressure of 4 bara and under conditions as in Table 2 (catalyst A, SV = 13,000 h⁻¹), increased activity was measured when the propane concentration was increased from 1500 to 2000 ppmv. Further increasing the propane/N₂O ratio had no further positive effect on the conversion of N₂O.

10

Experiments under conditions as in Table 2 (catalyst A, pressure = 4 bara, C₃H₈ concentration = 1900 ppmv) indicate that the space velocity can be increased from 13,000 to 45,000 h⁻¹ without the activity of the catalyst being adversely affected.

15

The stability of the catalyst is tested for 50 hours in the conditions as described in Table 2. No deterioration in the activity was detected.

V. N₂O conversion in different gas compositions

20

Table 5 demonstrates that the catalyst according to the present invention also functions well with higher water concentrations and higher oxygen concentrations. The table describes experiments in different gas compositions (conditions as in Table 2, catalyst B, SV = 13,000 h⁻¹, no NO and NO₂ present)

Table 5

Feed				Reaction T = 350°C	
N ₂ O (ppmv)	C ₃ H ₈ (ppmv)	O ₂ (% v/v)	H ₂ O (% v/v)	N ₂ O- conversion	CO (ppmv)
500	1000	6	0.5	97%	3
500	1000	3	0.5	97%	2
500	1000	2	0.5	84%	3
1000	1000	2	0.5	90%	2
1000	500	2	0.5	82%	2
500	1000	6	2	94%	2
1000 ^a	1000	2	0.5	73% ^a	1 ^a

^a In the presence of 250 ppmv NO

5

The catalyst X was tested in the presence of SO₂ (500 ppmv N₂O, 500 ppmv C₃H₈, 6% H₂O, 500 ppmv NO, 160 ppmv SO₂, SV = 6000 h⁻¹, T = 440-460°C). The catalyst is able to withstand sulphur: no deactivation was detected over a period of 550 hours under the above conditions.

CLAIMS

1. Method for the selective catalytic reduction of nitrous oxide (N_2O) in the presence of a solid catalyst, with the addition of a saturated hydrocarbon as reducing agent, characterized in that the catalyst used is a promoted iron-containing zeolite.
2. Method according to Claim 1, characterized in that the catalyst is promoted with a precious metal.
3. Method according to Claims 1 and 2, characterized in that the precious metal comprises ruthenium, rhodium, palladium, gold or platinum, or a combination of two or more of these metals.
4. Method according to Claim 1, characterized in that the reducing agent used is natural gas or methane (CH_4) or propane (C_3H_8) or LPG ($\text{C}_3\text{H}_8/\text{C}_4\text{H}_{10}$), or a combination thereof.
5. Method according to Claims 1 and 4, characterized in that the concentration of the reducing agent is set in such a way that the hydrocarbon/ N_2O molar ratio is in the range from 0.2 to 20, preferably in the range from 0.5 to 5.
6. Method according to Claim 1, characterized in that the reduction takes place at an inlet temperature of less than 400°C .
7. Method according to Claim 1, characterized in that the emission of carbonmonoxide (CO) and of hydrocarbon is in each case separately less than 100 ppmv.
8. Method according to Claim 1, characterized in that the process pressure at which the reduction takes place is between 1 and 50 bar absolute.

1/2

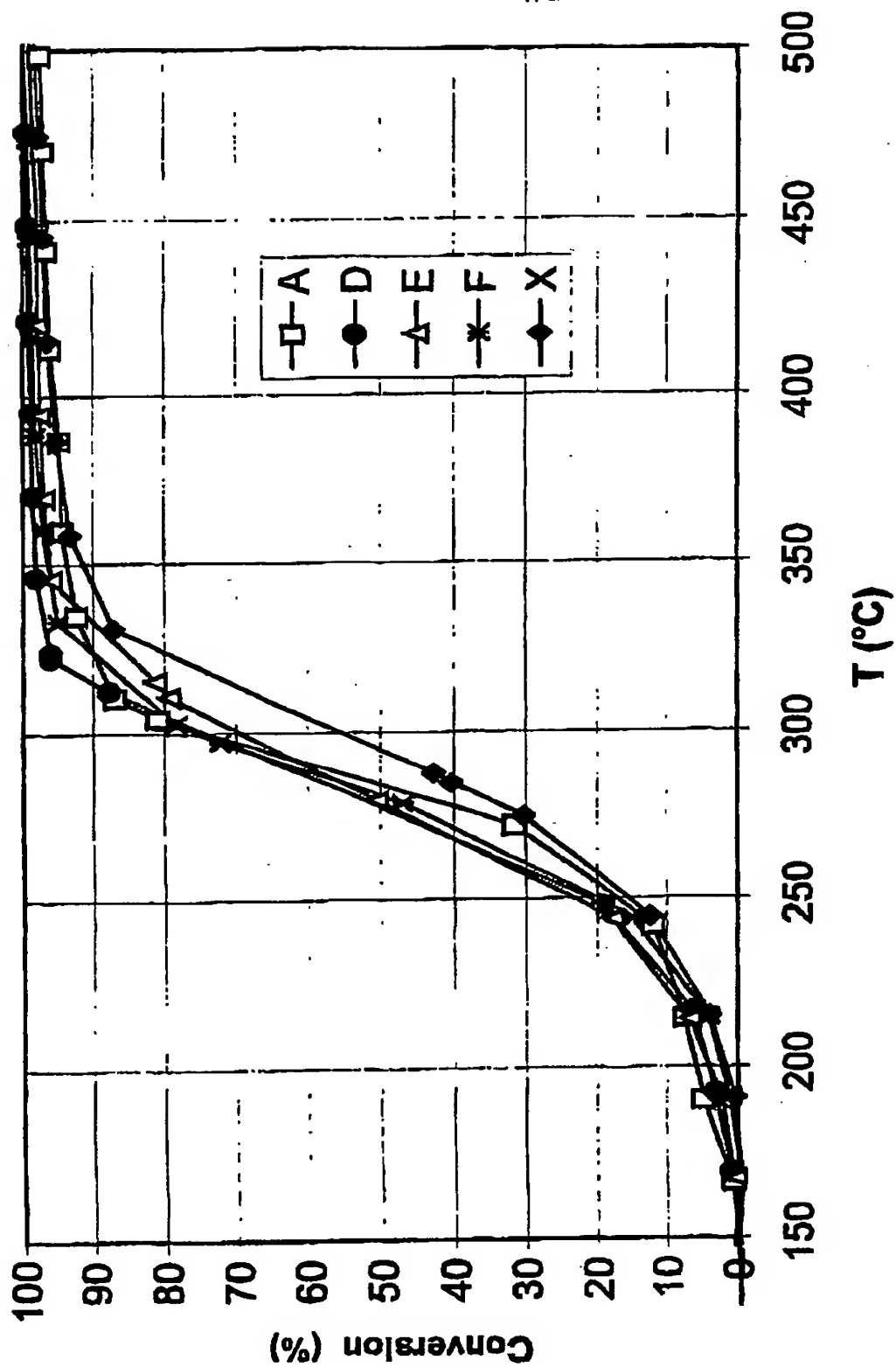


Fig. 1

2/2

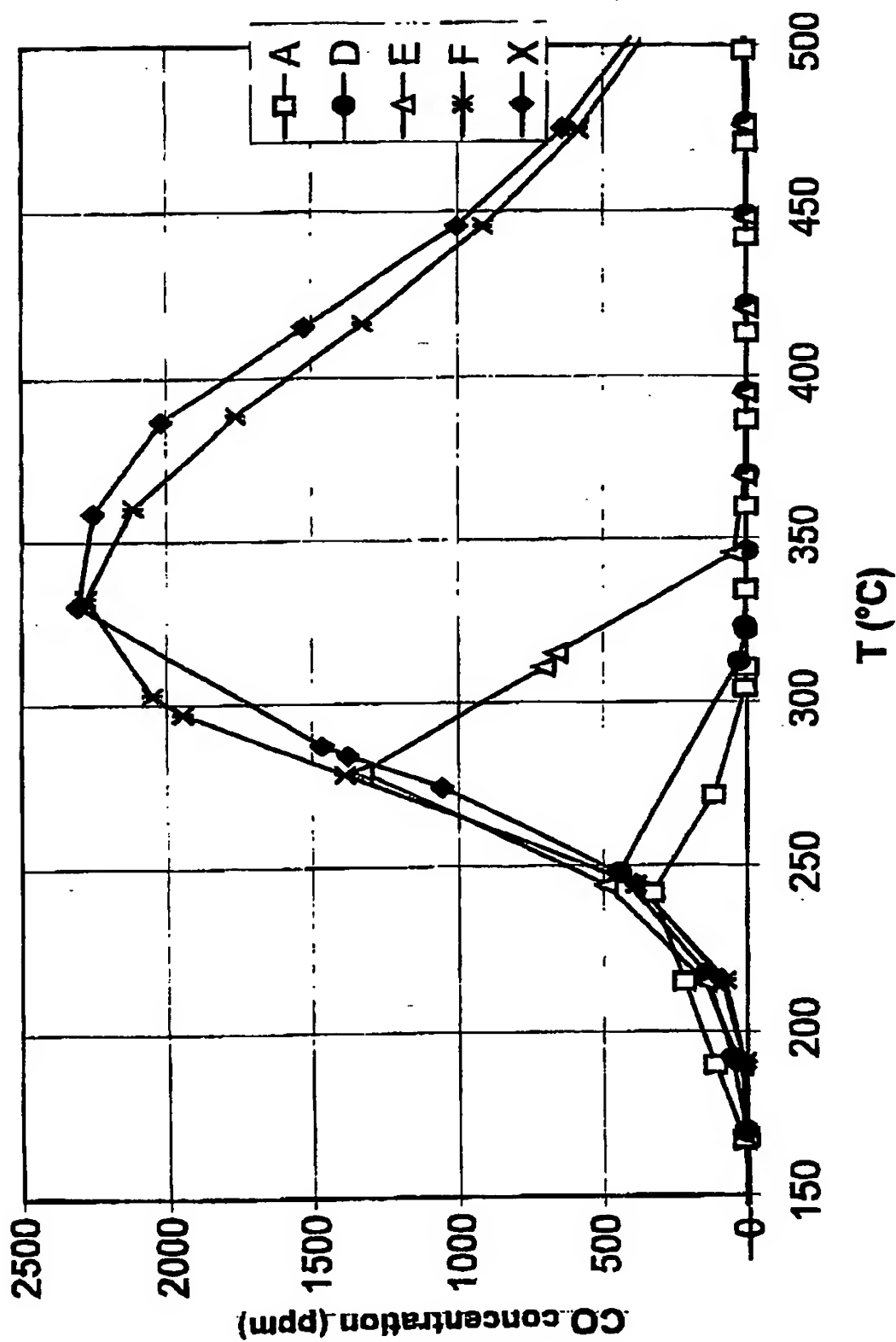


Fig. 2

INTERNATIONAL SEARCH REPORT

Ir. Application No
PCT/NL 00/00626

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 99 49954 A (STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND) 7 October 1999 (1999-10-07) cited in the application the whole document	1-8
A	US 5 524 432 A (JAMES G. HANSEL) 11 June 1996 (1996-06-11) column 7, line 15 - line 35	1-8
A	DE 41 28 629 A (BASF) 4 March 1993 (1993-03-04) the whole document	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

16 February 2001

Date of mailing of the international search report

23/02/2001

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00626

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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PCT/NL	00 / 00626
International Application No.	
(06.09.00)	6 Sep 2000
International Filing Date	
BUREAU VOOR DE INDUSTRIËLE EIGENDOM PCT. INTERNATIONAL APPLICATION	
Name of receiving Office and "PCT International Application"	
Applicant's or agent's file reference (if desired) (12 characters maximum) BO 42963 ABA	

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- ☐ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
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Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 06 SEP. 1999 (06.09.1999)	1012983	The Netherlands		
item (2) 15 DEC. 1999 (15.12.1999)	1013862	The Netherlands		
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1, 2

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ISA / EPO	Date (day/month/year)	Number	Country (or regional Office)
	28.06.2000	SN 34640 NL	The Netherlands

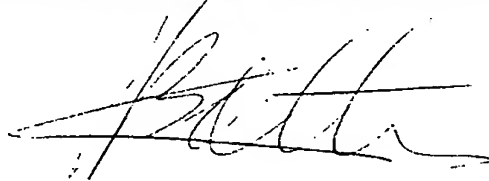
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This international application contains the following number of sheets: request : 3 description (excluding sequence listing part) : 8 claims : 1 abstract : 1 drawings : 2 sequence listing part of description : Total number of sheets : 15	This international application is accompanied by the item(s) marked below: 1. <input type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input checked="" type="checkbox"/> other (specify): copy search report
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Figure of the drawings which should accompany the abstract:	Language of filing of the international application: English
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BOTTEMA, Hans J.

Nederlandsch Octrooibureau, The Hague, 6 September 2000

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4. Date of timely receipt of the required corrections under PCT Article 11(2):	<input type="checkbox"/> not received:		
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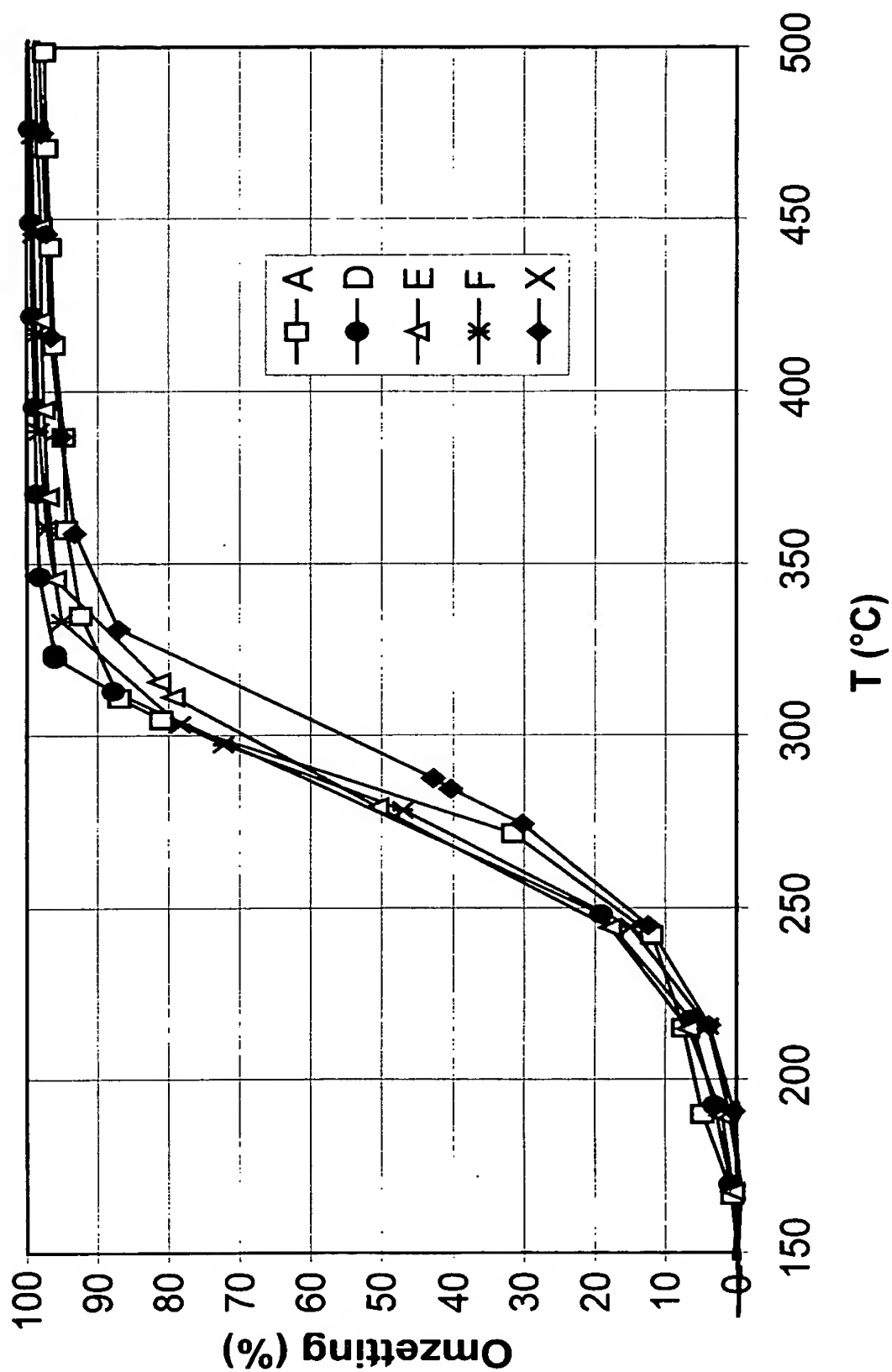


Fig. 1

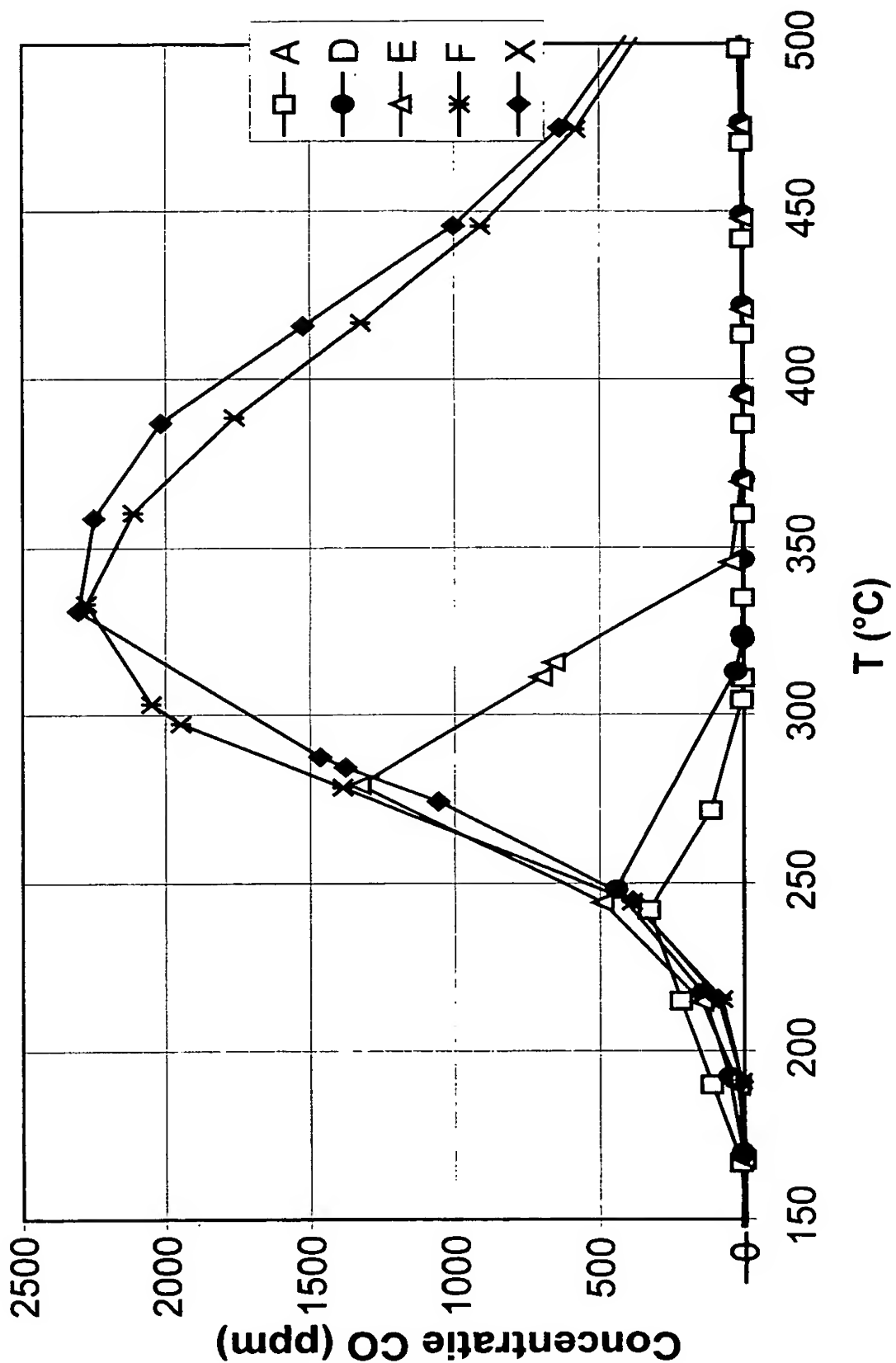


Fig. 2

Reductie van N₂O emissies

Achtergrond

Lachgas (distikstofoxide, N₂O) draagt sterk bij aan het broeikaseffect. De
5 *Global Warming Potential* (de mate waarin een molecule bijdraagt aan het
broeikaseffect ten opzichte van een molecule CO₂) van N₂O bedraagt ca. 310. Sinds
enkele jaren wordt er beleid ontwikkeld om de uitstoot van broeikasgassen terug te
dringen. De onderhavige uitvinding kan daartoe een belangrijke bijdrage leveren. Er
zijn verschillende belangrijke bronnen van N₂O emissie geïdentificeerd: de landbouw,
10 de industriële productie van precursors voor nylon (adipinezuur en caprolactam), de
productie van salpeterzuur en motorvoertuigen uitgerust met een driewegkatalysator.

Om lachgas onschadelijk te maken kunnen in principe verschillende
katalytische en niet-katalytische technieken aangewend worden. Voor de directe
katalytische decompositie van N₂O naar N₂ en O₂ zijn diverse katalysatoren bekend
15 (zie het literatuuroverzicht van Kapteijn *et al.*, Appl. Catal. B 9 (1996), p. 25-64 en
US-A-5,171,553). Deze reactie wordt echter sterk gehinderd door de aanwezigheid
van zuurstof en water, die in de afgassen van vrijwel alle voornoemde N₂O-bronnen
voorkomen. Een kansrijk alternatief is de selectieve katalytische reductie. Voor de
omzetting van N₂O met behulp van olefinen (C_nH_{2n}), alcoholen of ammonia zijn
20 diverse katalysatoren in de literatuur onderzocht (recentelijk: Mauzevin *et al.* Appl.
Catal. B 23 (1999) L79-L82 en Pophal *et al.* Appl. Catal. B 16 (1998) p. 177-186 en
de daarin geciteerde literatuur). Toegepaste katalysatoren zijn veelal zeolieten
uitgewisseld met een overgangsmetaal zoals ijzer, kobalt of koper.

Toevoeging van verzadigde koolwaterstoffen (C_nH_{2n+2}) zou technisch en
25 economisch de voorkeur verdienen boven voornoemde reductiemiddelen. Met name
aardgas (CH₄) en LPG (mengsel van C₃H₈ en C₄H₁₀) zijn in dit verband aantrekkelijk.
Belangrijk is hierbij dat vorming en emissie van koolmonoxide (CO) en emissie van
niet-gereageerde koolwaterstoffen geminimaliseerd wordt.

De onderhavige uitvinding betreft een katalysator waarmee N₂O bij relatief
30 lage temperatuur wordt omgezet in stikstof en waarmee zeer lage emissies van CO en
koolwaterstoffen worden bereikt.

Huidige stand der techniek

In de internationale octrooiaanvraag WO 9949954 is een werkwijze vastgelegd voor het katalytisch reduceren van N_2O in de aanwezigheid van een zeoliet onder de toevoeging van een reduceermiddel, waarbij als reduceermiddel een verzadigde koolwaterstof zoals methaan (CH_4), propaan (C_3H_8), LPG (C_3H_8/C_4H_{10}), of een combinatie van deze reduceermiddelen wordt toegepast. Gebleken is dat bij reactie temperaturen van $400^\circ C$ of lager volledige omzetting van N_2O kan worden bereikt zelfs bij zeer lage concentraties van het reduceermiddel en in de aanwezigheid van waterdamp, zuurstof en zwaveldioxide. De katalysator betreft een speciaal bereide met ijzer uitgewisselde zeoliet.

De Japanse patent publicaties JP 05103953 en JP 07213864 beschrijven N_2O -verwijdering in aanwezigheid van respectievelijk methaan en propaan met behulp van (onder andere) een ijzer-zeoliet katalysator. Deze werkwijzen houden echter geen rekening met emissie van CO en niet-gereageerde koolwaterstoffen.

Om de ongewenste emissie van CO en rest-koolwaterstoffen te voorkomen beschrijft de Japanse patentpublicatie JP 09000884 de mechanische menging van een ijzer-zeoliet katalysator met een gedragen platina- of palladiumkatalysator. De N_2O -omzetting ligt rond de 60% bij $450^\circ C$ in een zuurstof en waterhoudend gas. De omzetting van N_2O met de mechanisch gemengde katalysator is beduidend slechter dan met de ijzer-zeoliet katalysator alleen.

Zowel in JP 05103953, JP 07213864 als in JP 09000884 ontbreekt informatie over de werkzaamheid van de uitvinding onder druk en/of in aanwezigheid van zwavel verbindingen. Dit is essentieel voor toepassing in respectievelijk de salpeterzuur- en caprolactamproductie.

Ontdekking nieuwe katalysator

Het is een doel van de onderhavige uitvinding te voorzien in een werkwijze voor de verwijdering van N_2O uit O_2 -, H_2O -, NO_x - en eventueel zwavelhoudende industriële gasstromen, welke zich eventueel onder druk bevinden. Het is een verder doel van de onderhavige uitvinding om de voornoemde verwijdering van N_2O te bewerkstelligen door toevoeging van verzadigde koolwaterstoffen bij een reactie temperatuur lager dan $400^\circ C$ waarbij een zeer lage emissie van CO en niet-gereageerde koolwaterstoffen wordt bewerkstelligd.

Hiertoe is de werkwijze volgens de uitvinding gekenmerkt doordat als katalysator een gepromoteerde, ijzerhoudende zeoliet wordt toegepast. Bij voorkeur is de zeoliet katalysator gepromoteerd met een edelmetaal.

5 De toepassing van een bij voorkeur met edelmetaal (Rh, Pd, Ru, Pt, Au, etc.) gepromoteerde ijzerbevattende zeoliet katalysator in de SCR van N_2O met behulp van verzadigde koolwaterstoffen (C_nH_{2n+2}) leidde verrassenderwijs tot een verhoogde omzetting van N_2O in vergelijking tot een niet-gepromoteerde ijzerbevattende zeoliet katalysator. De gepromoteerde katalysator is actief beneden de $350^\circ C$.

10 Verder is gebleken dat de met edelmetaal gepromoteerde ijzerbevattende zeoliet katalysator de emissie van CO en van rest-koolwaterstoffen bij bedrijfstemperatuur zeer sterk verlaagd ten opzichte van een niet-gepromoteerde ijzerbevattende zeoliet katalysator.

15 Nog verder is gebleken dat de katalysator volgens de onderhavige uitvinding eveneens actief is in de verwijdering van stikstofoxiden ($NO + NO_2 = NO_x$). Dit is een belangrijk gegeven in verband met het feit dat met de verschillende bronnen van N_2O ook NO_x vrijkomen.

20 Tevens is gebleken dat de beschreven katalysator eveneens zeer actief is in de beoogde omzetting onder verhoogde procesdruk en zelfs actiever is dan bij atmosferische druk. Dit is een belangrijk gegeven in verband met toepassing in de salpeterzuur industrie.

Tenslotte is gebleken dat de beschreven katalysator actief is wanneer zwavel in de voeding aanwezig is. Dit is een belangrijk gegeven in verband met toepassing in de nylon industrie.

25 De uitvinding zal nader uiteen worden gezet aan de hand van de hiernavolgende voorbeelden samen met de bijbehorende figuren.

Hierin toont:

30 Figuur 1 de omzettingsgraad van N_2O als functie van de temperatuur van vier met edelmetaal gepromoteerde ijzerbevattende zeoliet katalysatoren (A, D, E en F). Ter vergelijking is ook de N_2O omzetting van een niet-gepromoteerde ijzerbevattende zeoliet katalysator (X) afgebeeld. De testcondities zijn beschreven in Tabel 2 ($SV = 19.500 \text{ hr}^{-1}$, druk = 3 bara, C_3H_8 -concentratie = 1900 ppmv).

Figuur 2 de CO emissie die optreedt bij de omzetting van N₂O onder gebruikmaking van dezelfde katalysatoren en onder dezelfde condities als in Figuur 1.

I. Bereiding van de katalysatoren

De katalysatoren volgens de onderhavige uitvinding worden vervaardigd door het toevoegen van zeoliet Na-ZSM-5 of NH₄-ZSM-5 aan een oplossing van (NH₄)₂Fe(SO₄)₂·6H₂O (Mohr's zout). Na samenvoeging wordt een ionenuitwisseling uitgevoerd bij 80°C gedurende 8 uur. De resulterende suspensie wordt afgefiltreerd, het vaste materiaal gewassen, gedroogd bij 80°C en gecalcineerd bij 550°C.

Het zo verkregen Fe-ZSM-5 basismateriaal wordt vervolgens geïmpregneerd met een zodanig volume van een oplossing van een edelmetaalprecursor in gedemineraliseerd water opdat de poriën van het basismateriaal precies gevuld worden (zogenaamde *incipient wetness impregnation*). De concentratie van de edelmetaalprecursor wordt zodanig ingesteld dat de gewenste hoeveelheid edelmetaal op het basismateriaal wordt verkregen. Tenslotte wordt de katalysator gedroogd bij 80°C en gecalcineerd bij 550°C. Het verkregen katalysatorpoeder wordt tot een pil geperst, vermalen en gezeefd.

De volgende katalysatoren worden gebruikt in de voorbeelden:

Tabel 1.

Katalysator	Basis	Edelmetaal
A	Fe-ZSM-5 ex Mohr's zout	0.05% Pd
B	Fe-ZSM-5 ex Mohr's zout	0.1% Pd
C	Fe-ZSM-5 ex Mohr's zout	0.3% Pd
D	Fe-ZSM-5 ex Mohr's zout	0.3% Rh
E	Fe-ZSM-5 ex Mohr's zout	0.3% Ru
F	Fe-ZSM-5 ex Mohr's zout	0.3% Au
X	Fe-ZSM-5 ex Mohr's zout	geen

II. Testapparatuur

De omzetting van N₂O middels SCR met propaan en methaan werd bestudeerd in een geautomatiseerde flow opstelling. De gassen N₂, lucht, N₂O, C₃H₈, CH₄, NO,

NO₂ worden geïntroduceerd door middel van gekalibreerde Massa Flow Controllers (Brooks). Water wordt toegevoegd via een Liquiflow controller en een Controlled Evaporator Mixer (Bronkhorst). De analyse van de uitstromende gassen vindt plaats door middel van een gekalibreerde FTIR-spectrofotometer (Elsag, Bailey, Hartmann & Braun, type MB 100). De katalysator bevindt zich in een roestvrijstalen reactor. De gassen worden door een voorverwarmingsectie geleid voordat ze met de katalysator in aanraking komen. De temperatuur wordt aan de ingang en aan de uitgang van het katalysatorbed gemeten met thermokoppels. In de resultaten van de tests wordt het gemiddelde van deze twee temperaturen weergegeven. De druk in de testopstelling kan ingesteld worden op waarden tussen 1 en 5 bar absoluut (bara).

De gassamenstelling in de voorbeelden is representatief voor toepassing van de katalysator volgens de onderhavige uitvinding in de salpeterzuurindustrie. De algemene testcondities zijn:

Tabel 2.

Gewicht katalysator	6 - 15 g
Zeeffractie	0,71 - 1,4 mm
Volume katalysator	10 - 23 ml
Totaal gasdebiet	5 - 7,5 liter/min (STP)
Space Velocity	13.000 - 45.000 hr ⁻¹
Totale druk	1 - 5 bara
Temperatuur katalysator	150 - 500 °C
O ₂ -concentratie	2,5 % v/v
H ₂ O-concentratie	0,5% v/v
N ₂ O-concentratie	1500 ppmv
C ₃ H ₈ -concentratie	1500 - 2500 ppmv
NO ₂ -concentratie	100 ppmv
NO-concentratie	100 ppmv

III. Invloed van de toevoeging van edelmetaal aan ijzerbevattend zeoliet

Figuur 1 toont de N₂O-omzettingcurves voor de katalysatoren uit Tabel 1 (testcondities als in Tabel 2, SV = 19.500 hr⁻¹, druk = 3 bara, C₃H₈-concentratie = 1900 ppmv). De gepromoteerde katalysatoren (A,D,E,F) zijn actiever dan de niet-

gepromoteerde ijzerbevattende zeoliet katalysator X. Dat blijkt uit het verschuiven van de N_2O -conversiecurves naar lagere temperatuur ten opzichte van de niet-gepromoteerde Fe-ZSM-5 katalysator X.

Figuur 2 toont van diezelfde katalysatoren, onder dezelfde condities, de CO concentraties tegen de temperatuur. Bij toepassing van katalysator X en van katalysator F vindt er in het gehele temperatuurgebied CO vorming plaats. De andere katalysatoren zijn in staat CO-uitstoot uitstekend te elimineren: bij toepassing van katalysator E is de hoeveelheid CO boven de 350°C lager dan 10 ppmv en bij katalysatoren A en D is dit al vanaf 300°C het geval.

Vergelijkende tests van katalysator A (met 0,05% Pd) met katalysatoren B en C (met resp. 0,1% en 0,3% Pd) laten gelijke curven voor zowel N_2O -conversie als CO-vorming zien. Dit betekent dat met een lage edelmetaalconcentratie volstaan kan worden, wat de katalysator goedkoper maakt.

Tabel 3 toont van een aantal katalysatoren de concentraties van de verbindingen die de reactor verlaten bij een gemiddelde temperatuur van 350°C (testcondities als in Tabel 2, $SV = 19.500 \text{ hr}^{-1}$, druk = 3 bara, C_3H_8 -concentratie = 1900 ppmv).

Tabel 3.

Katalysator	N_2O (ppmv)	C_3H_8 (ppmv)	CO (ppmv)	NO_x^a (ppmv)
C	70	62	3	85
D	55	33	1	85
E	130	75	37	82
F	42	70	2180	45
X	123	167	2267	46

^a $NO_x = NO + NO_2$

Voor alle katalysatoren is de N_2O - en de C_3H_8 -conversie hoger dan 90% bij 350°C . Voor de Pd en Rh bevattende katalysatoren is de CO-emissie nihil. Verrassend is dat de katalysatoren ook een NO_x -verwijderingsgraad van 60 tot 75% bereiken.

IV. Activiteit van de gepromoteerde ijzerbevattende zeoliet katalysatoren bij verhoogde procesdruk en space velocity.

Verhoging van de procesdruk heeft een gunstig effect op de activiteit van de katalysatoren. Tabel 4 toont de concentraties van een aantal componenten in het uitstromende gas gegeven bij 1, 3 en 5 bara en bij een reactietemperatuur van 350°C (testcondities als in Tabel 2, Katalysator A, $SV = 19.500 \text{ hr}^{-1}$, C_3H_8 -concentratie = 1900 ppmv). De N_2O -conversie blijft groter dan 90%, propaan-slip, CO- en NO_x -emissies nemen af met toenemende procesdruk.

Tabel 4.

druk (bara)	N_2O (ppmv)	C_3H_8 (ppmv)	CO (ppmv)	NO_x^a (ppmv)
1	95	200	14	137
3	128	124	3	135
5	100	54	2	122

^a $NO_x = NO + NO_2$

Bij een procesdruk van 4 bara en condities zoals in Tabel 2 (katalysator A, $SV = 13.000 \text{ hr}^{-1}$) werd een verhoogde activiteit gemeten bij verhoging van de propaanconcentratie van 1500 naar 2000 ppmv. Verdere verhoging van de propaan/ N_2O verhouding heeft geen verder positief effect op de omzetting van N_2O .

Experimenten bij condities zoals in Tabel 2 (katalysator A, druk = 4 bara, C_3H_8 -concentratie = 1900 ppmv) geven aan dat de space velocity verhoogd kan worden van 13.000 naar 45.000 hr^{-1} met behoud van de activiteit van de katalysator.

De stabiliteit van de katalysator is voor 50 uur getest in de condities zoals beschreven in Tabel 2. Geen afname van de activiteit werd waargenomen.

V. N_2O -omzetting in afwijkende gassenstelling

Tabel 5 toont dat de katalysator volgens de onderhavige uitvinding ook goed functioneert bij hogere waterconcentraties en hogere zuurstofconcentraties. De Tabel beschrijft experimenten in afwijkende gassenstelling (condities als in Tabel 2, katalysator B, $SV = 13.000 \text{ hr}^{-1}$, NO en NO_2 afwezig).

Tabel 5.

Invoer				Reactie T = 350°C	
N ₂ O (ppmv)	C ₃ H ₈ (ppmv)	O ₂ (% v/v)	H ₂ O (% v/v)	N ₂ O-conversie	CO (ppmv)
500	1000	6	0.5	97%	3
500	1000	3	0.5	97%	2
500	1000	2	0.5	84%	3
1000	1000	2	0.5	90%	2
1000	500	2	0.5	82%	2
500	1000	6	2	94%	2
1000 ^a	1000	2	0.5	73% ^a	1 ^a

^a In aanwezigheid van 250 ppmv NO.

5 De katalysator X is getest in aanwezigheid van SO₂ (500 ppmv N₂O, 500 ppmv C₃H₈, 6% O₂, 6% H₂O, 500 ppmv NO, 160 ppmv SO₂, SV = 6.000 hr⁻¹, T = 440 – 460 °C). De katalysator is bestand tegen zwavel: in een periode van 550 uur in voornoemde condities werd geen deactivering waargenomen.

Conclusies

1. Werkwijze voor het selectief katalytisch reduceren van lachgas (N_2O) in de aanwezigheid van een vaste katalysator onder toevoeging van een verzadigde koolwaterstof als reduceermiddel, met het kenmerk dat als katalysator een gepromoteerde, ijzerbevattende zeoliet wordt toegepast.
2. Werkwijze volgens conclusie 1, met het kenmerk dat de katalysator gepromoteerd is met een edelmetaal.
3. Werkwijze volgens conclusies 1 en 2, met het kenmerk dat het edelmetaal ruthenium, rhodium, palladium, goud of platina, of een combinatie van twee of meerdere van deze metalen, omvat.
4. Werkwijze volgens conclusie 1, met het kenmerk dat als reduceermiddel aardgas of methaan (CH_4) of propaan (C_3H_8) of LPG (C_3H_8/C_4H_{10}) wordt toegepast, of een combinatie daarvan.
5. Werkwijze volgens conclusies 1 en 4, met het kenmerk dat de concentratie van het reduceermiddel zodanig wordt ingesteld dat de molaire koolwaterstof/ N_2O verhouding in het gebied ligt van 0,2 tot 20 en bij voorkeur in het gebied ligt van 0,5 tot 5.
6. Werkwijze volgens conclusie 1, met het kenmerk dat de reductie plaats vindt bij een inlaattemperatuur van minder dan $400^{\circ}C$.
7. Werkwijze volgens conclusie 1, met het kenmerk dat emissie van koolmonoxide (CO) en van koolwaterstof ieder afzonderlijk minder dan 100 ppmv is.
8. Werkwijze volgens conclusies 1, met het kenmerk dat de procesdruk waarbij de reductie plaats vindt tussen 1 en 50 bar absoluut is.

UITTREKSEL

De uitvinding betreft een werkwijze voor het selectief katalytisch reduceren van lachgas (N_2O) in de aanwezigheid van een vaste katalysator onder toevoeging van een verzadigde koolwaterstof als reduceermiddel. De uitvinding is gekenmerkt doordat als katalysator een gepromoteerde, ijzerbevattende zeoliet wordt toegepast. Hierdoor kan een verhoogde omzetting van NO_2 worden verkregen in vergelijking met niet-gepromoteerde ijzerbevattende zeoliet katalysatoren. De gepromoteerde katalysator volgens de uitvinding is actief beneden 350°C . Verder is gebleken dat de met edelmetaal gepromoteerde ijzerbevattende zeoliet katalysatoren een lage emissie van CO en rest-koolwaterstoffen hebben. Tevens is de katalysator zeer actief bij hoge procesdrukken en in de aanwezigheid van zwavel.